

[μ -3-(Methylsulfanyl)benzene-1,2-di-thiolato-1:2 κ^4 S,S':S,S']bis[tricarbonyl-iron(I)]

Yong Yang,^a Ning Wang^{b*} and Lin Chen^a

^aState Key Laboratory of Fine Chemicals, Dalian University of Technology (DUT), Dalian 116024, People's Republic of China, and ^bSchool of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, People's Republic of China

Correspondence e-mail: ssdyok@yahoo.com.cn

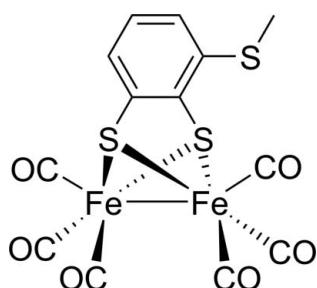
Received 22 March 2013; accepted 10 April 2013

Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.036; wR factor = 0.084; data-to-parameter ratio = 13.9.

The title compound, $[\text{Fe}_2(\text{C}_7\text{H}_6\text{S}_3)(\text{CO})_6]$, was prepared as a biomimic for the active site of [FeFe]-hydrogenases. The central Fe_2S_2 core is in a butterfly conformation and each Fe^{I} atom has a pseudo-square-pyramidal coordination by three O atoms and two S atoms. The $\text{Fe}-\text{Fe}$ distance is 2.471 (2) Å and the dihedral angle between the two $\text{Fe}-\text{S}-\text{Fe}$ planes is 78.96 (7)°. The least-squares plane through the $-\text{S}(\text{C}_7\text{H}_6\text{S})\text{S}-$ bridge nearly bisects the molecular structure: except for the two $\text{Fe}(\text{CO})_3$ units, all atoms are in this plane with an average deviation from the plane of 0.028 (3) Å. In the crystal, the molecules are linked into chains along [001] by $\text{C}-\text{H}\cdots\pi(\text{arene})$ interactions.

Related literature

For general background to [FeFe]-hydrogenases, see: Capon *et al.* (2009); Tard & Pickett (2009). For the crystal structure of the natural enzyme, see: Peters *et al.* (1998); Nicolet *et al.* (1999). For related structures and the synthesis, see: Maiolo *et al.* (1981); Wang *et al.* (2005); Dong *et al.* (2006).



Experimental

Crystal data

$[\text{Fe}_2(\text{C}_7\text{H}_6\text{S}_3)(\text{CO})_6]$
 $M_r = 466.06$
Monoclinic, $P2_1/c$
 $a = 16.531$ (17) Å
 $b = 7.975$ (8) Å
 $c = 13.047$ (13) Å
 $\beta = 92.055$ (13)°

$V = 1719$ (3) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 2.08$ mm⁻¹
 $T = 295$ K
 $0.39 \times 0.24 \times 0.08$ mm

Data collection

Bruker APEXII CCD
diffractometer
Absorption correction: multi-scan
(SADABS; Bruker, 2001)
 $T_{\min} = 0.555$, $T_{\max} = 0.847$

8260 measured reflections
3024 independent reflections
2098 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.084$
 $S = 0.97$
3024 reflections

217 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.44$ e Å⁻³
 $\Delta\rho_{\min} = -0.31$ e Å⁻³

Table 1
Selected bond lengths (Å).

Fe1—C1	1.789 (5)	Fe2—C4	1.789 (5)
Fe1—C2	1.786 (4)	Fe2—C5	1.781 (4)
Fe1—C3	1.788 (5)	Fe2—C6	1.784 (5)
Fe1—S1	2.2695 (19)	Fe2—S1	2.2763 (19)
Fe1—S2	2.253 (2)	Fe2—S2	2.263 (2)

Table 2
C—H···π(arene) interaction geometry (Å, °).

$Cg1$ is the centroid of the C7–C12 ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
C13—H13A··· $Cg1^i$	0.96	2.69	3.590 (5)	157

Symmetry code: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

We are grateful to the Chinese National Natural Science Foundation (grant No. 21101057), the Doctoral Fund of Henan University of Technology (No. 2009BS053) and the Science Foundation of the Education Department of Henan Province (No. 2011B150006) for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: VN2067).

References

Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *SAINT-Plus* and *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.

metal-organic compounds

Capon, J.-F., Gloaguen, F., Pétillon, F. Y., Schollhammer, P. & Talarmin, J. (2009). *Coord. Chem. Rev.* **253**, 1476–1494.

Dong, W., Wang, M., Liu, X., Jin, K., Li, G., Wang, F. & Sun, L. (2006). *Chem. Commun.* pp. 305–307.

Maiolo, F., Testaferri, L., Tiecco, M. & Tingoli, M. (1981). *J. Org. Chem.* **46**, 3070–3073.

Nicolet, Y., Piras, C., Legrand, P., Hatchikian, C. E. & Fontecilla-Camps, J. C. (1999). *Structure*, **7**, 13–23.

Peters, J. W., Lanzilotta, W. N., Lemon, B. J. & Seefeldt, L. C. (1998). *Science* **282**, 1853–1858.

Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.

Tard, C. & Pickett, C. J. (2009). *Chem. Rev.* **109**, 2245–2274.

Wang, F., Wang, M., Liu, X., Jin, K., Dong, W., Li, G., Åkermark, B. & Sun, L. (2005). *Chem. Commun.* pp. 3221–3223.

supplementary materials

Acta Cryst. (2013). **E69**, m269–m270 [doi:10.1107/S1600536813009860]

[μ -3-(Methylsulfanyl)benzene-1,2-dithiolato-1:2 κ^4 S,S':S,S']bis[tricarbonyl-iron(I)]

Yong Yang, Ning Wang and Lin Chen

Comment

[FeFe]-hydrogenases are important enzymes in numerous microorganisms, which can catalyse hydrogen evolution or uptake. Crystallographic and IR spectroscopic studies on the two types of [FeFe]Hases, CpI (*Clostridium pasteurianum*) and DdH (*Desulfovibrio desulfuricans*), revealed that the active site of [FeFe]-hydrogenases is comprised of a 2Fe2S butterfly structure, which contains diatomic ligands CO and CN[−], a cysteinyl-S ligand connecting to a 4Fe4S subcluster, and a three-atom linker (−CH₂XCH₂−, X = CH₂, NH or O) bridged between the two S atoms of the Fe₂S₂ H-cluster (Capon *et al.*, 2009, Tard & Pickett, 2009). It was found that the introduction of a rigid and conjugate bridge to the Fe₂S₂ complexes could make the electrochemical properties of the complexes apparently different from the Fe₂S₂ complexes with flexible bridges (Capon *et al.*, 2009).

The structure of the title compound resembles the active site of [FeFe]-hydrogenases, with a butterfly architectonic 2Fe2S core and the usual distorted square-pyramidal geometry around the iron center (Wang *et al.*, 2005, Dong *et al.*, 2006). The length of the Fe–Fe bond [2.471 (2) Å] is slightly shorter than those in the structures of natural enzymes (*ca* 2.6 Å) (Peters *et al.*, 1998, Nicolet *et al.*, 1999). The dihedral angle between two Fe–S–Fe planes is 78.96 (7) °. The rigid dithiolate bridge is a special feature for the title compound. The molecular structure has an internal pseudo-mirror plane passing through the aromatic ring. The calculated plane of the SRS bridge is nearly a bisecting plane of the molecular structure. Except for two Fe(CO)₃ units all atoms are in the plane with the average deviation of 0.0280 Å. The deviations of the iron atoms from the SRS basal plane are 1.266 (5) Å for Fe(1) and 1.205 (5) Å for Fe(2). The molecular structure of the title compound is shown in Figure 1.

Experimental

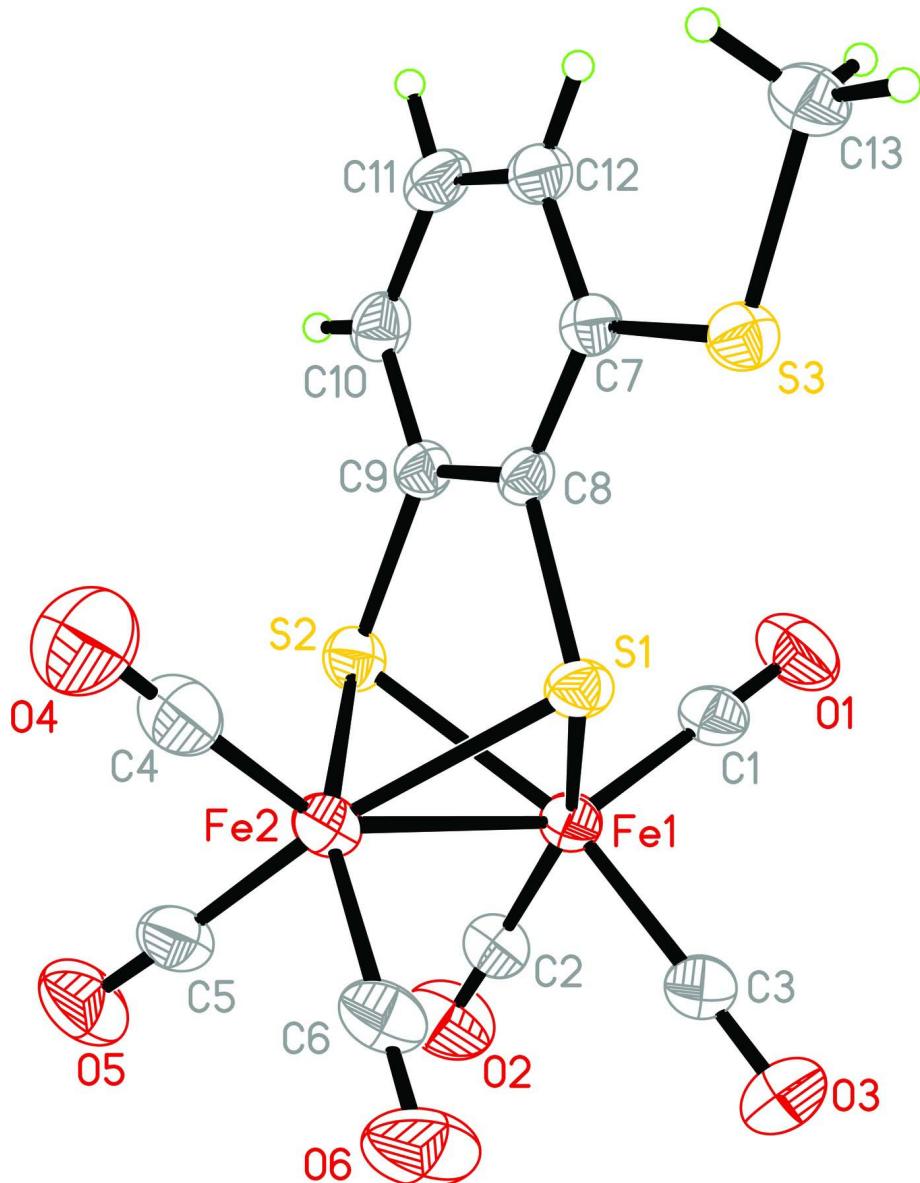
All reactions and operations related to the title compound were carried out under a dry, prepurified nitrogen atmosphere with standard Schlenk techniques. All solvents were dried and distilled prior to use according to standard methods. The starting material 3-(methylthio)benzene-1,2-dilthiol was prepared by a similar procedure according to the literature (Maiolo *et al.*, 1981). 3-(Methylthio)benzene-1,2-dilthiol (1 mmol, 0.188 g) and freshly synthesized Fe₃(CO)₁₂ (1 mmol, 0.503 g) were refluxed in toluene under N₂ atmosphere for 3 h. The color of the solution changed gradually from dark green to dark red. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane as eluent to give the title compound as a red solid (0.294 g, 63%). A single-crystal suitable for X-ray study was obtained by slow evaporation of CH₂Cl₂/hexane (1:10, *v/v*) solution at room temperature. IR (CH₂Cl₂, cm^{−1}): ν (CO) 2075 (*m*), 2045 (*s*), 1999 (*versus*); ¹H NMR (400 MHz, CDCl₃): δ 6.92 (*s*, 1H, C₆H₃), 6.60 (*s*, 1H, C₆H₃), 6.53 (*s*, 1H, C₆H₃), 2.41 (*s*, 3H, SCH₃).

Refinement

Hydrogen atoms were positioned geometrically and refined as riding atoms, with C–H = 0.93 (CH) and 0.96 (CH₃) Å and with $U_{\text{iso}}(\text{H}) = 1.2$ (1.5 for methyl) $U_{\text{eq}}(\text{C})$.

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

**Figure 1**

Molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.

[μ -3-(Methylsulfanyl)benzene-1,2-dithiolato-1:2 κ^4 S,S':S,S']bis[tricarbonyliron(I)]

Crystal data

[Fe₂(C₇H₆S₃)(CO)₆] $M_r = 466.06$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 16.531$ (17) Å $b = 7.975$ (8) Å $c = 13.047$ (13) Å $\beta = 92.055$ (13)° $V = 1719$ (3) Å³ $Z = 4$ $F(000) = 928$ $D_x = 1.801$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2629 reflections

 $\theta = 2.5\text{--}27.1^\circ$ $\mu = 2.08$ mm⁻¹ $T = 295$ K

Block, red

0.39 × 0.24 × 0.08 mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2001)

 $T_{\min} = 0.555$, $T_{\max} = 0.847$

8260 measured reflections

3024 independent reflections

2098 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.055$ $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.5^\circ$ $h = -19\text{--}18$ $k = -9\text{--}9$ $l = -15\text{--}13$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.036$ $wR(F^2) = 0.084$ $S = 0.97$

3024 reflections

217 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0341P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.44$ e Å⁻³ $\Delta\rho_{\min} = -0.31$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\text{iso}}^* / U_{\text{eq}}$
Fe1	0.17590 (2)	0.29795 (7)	0.64150 (4)	0.04642 (17)
Fe2	0.18906 (3)	0.54555 (7)	0.52941 (4)	0.04814 (18)
S3	0.46296 (5)	0.53167 (12)	0.73543 (7)	0.0462 (2)
S2	0.22860 (5)	0.28468 (12)	0.48479 (7)	0.0475 (2)
S1	0.27674 (5)	0.48911 (12)	0.66349 (7)	0.0446 (2)

C8	0.35707 (16)	0.3899 (4)	0.5983 (2)	0.0354 (7)
C10	0.3893 (2)	0.2051 (4)	0.4606 (3)	0.0481 (9)
H10A	0.3730	0.1375	0.4055	0.058*
C2	0.0831 (2)	0.2118 (5)	0.5909 (3)	0.0560 (10)
C9	0.33421 (18)	0.2915 (4)	0.5159 (3)	0.0401 (8)
C5	0.1075 (2)	0.5260 (5)	0.4373 (4)	0.0605 (11)
C1	0.21760 (19)	0.1120 (6)	0.6991 (3)	0.0564 (10)
C7	0.43793 (17)	0.4062 (4)	0.6280 (3)	0.0377 (8)
C11	0.4698 (2)	0.2221 (5)	0.4897 (3)	0.0514 (9)
H11A	0.5086	0.1648	0.4535	0.062*
C12	0.49397 (19)	0.3216 (4)	0.5709 (3)	0.0449 (9)
H12A	0.5488	0.3324	0.5879	0.054*
O2	0.02428 (15)	0.1593 (4)	0.5570 (3)	0.0859 (10)
O1	0.24308 (17)	-0.0076 (4)	0.7338 (3)	0.0867 (11)
C4	0.2506 (2)	0.6882 (6)	0.4606 (4)	0.0700 (12)
O5	0.05695 (18)	0.5075 (4)	0.3771 (3)	0.0918 (11)
O6	0.09707 (19)	0.7802 (4)	0.6518 (3)	0.0961 (12)
O4	0.2905 (2)	0.7821 (5)	0.4201 (3)	0.1088 (13)
O3	0.09360 (19)	0.4359 (5)	0.8164 (3)	0.0994 (12)
C6	0.1338 (2)	0.6903 (5)	0.6042 (4)	0.0643 (12)
C3	0.1254 (2)	0.3805 (6)	0.7494 (4)	0.0631 (11)
C13	0.57037 (19)	0.5072 (4)	0.7506 (3)	0.0543 (10)
H13A	0.5900	0.5721	0.8082	0.082*
H13B	0.5956	0.5454	0.6897	0.082*
H13C	0.5831	0.3911	0.7619	0.082*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0379 (3)	0.0561 (4)	0.0452 (3)	-0.0011 (2)	0.0000 (2)	0.0002 (3)
Fe2	0.0429 (3)	0.0491 (4)	0.0522 (4)	0.0050 (2)	-0.0029 (2)	-0.0011 (3)
S3	0.0421 (4)	0.0487 (6)	0.0479 (6)	-0.0040 (4)	0.0011 (4)	-0.0067 (5)
S2	0.0480 (4)	0.0519 (6)	0.0422 (6)	-0.0004 (4)	-0.0046 (4)	-0.0077 (5)
S1	0.0379 (4)	0.0538 (6)	0.0423 (6)	0.0033 (4)	0.0016 (4)	-0.0123 (4)
C8	0.0392 (15)	0.036 (2)	0.0313 (19)	0.0026 (15)	0.0060 (13)	-0.0023 (16)
C10	0.061 (2)	0.046 (2)	0.038 (2)	0.0035 (18)	0.0044 (17)	-0.0051 (18)
C2	0.052 (2)	0.058 (3)	0.057 (3)	0.0055 (19)	-0.0012 (18)	0.002 (2)
C9	0.0433 (16)	0.040 (2)	0.037 (2)	0.0048 (15)	0.0035 (14)	0.0003 (17)
C5	0.052 (2)	0.061 (3)	0.068 (3)	0.0124 (19)	-0.001 (2)	-0.002 (2)
C1	0.0372 (17)	0.070 (3)	0.061 (3)	-0.0023 (19)	-0.0012 (17)	-0.001 (2)
C7	0.0405 (16)	0.0300 (19)	0.043 (2)	-0.0003 (14)	0.0051 (14)	0.0067 (16)
C11	0.056 (2)	0.050 (2)	0.050 (3)	0.0106 (18)	0.0194 (17)	0.003 (2)
C12	0.0416 (17)	0.046 (2)	0.048 (2)	0.0045 (16)	0.0079 (15)	0.0058 (19)
O2	0.0549 (15)	0.087 (2)	0.115 (3)	-0.0205 (15)	-0.0156 (17)	-0.004 (2)
O1	0.0665 (18)	0.085 (2)	0.108 (3)	0.0094 (17)	-0.0127 (18)	0.028 (2)
C4	0.062 (2)	0.069 (3)	0.079 (3)	0.006 (2)	-0.005 (2)	0.006 (3)
O5	0.0720 (19)	0.109 (3)	0.092 (3)	0.0123 (17)	-0.034 (2)	-0.008 (2)
O6	0.083 (2)	0.088 (3)	0.117 (3)	0.0311 (18)	-0.0015 (19)	-0.043 (2)
O4	0.101 (2)	0.096 (3)	0.130 (4)	-0.025 (2)	0.021 (2)	0.030 (3)
O3	0.087 (2)	0.145 (3)	0.068 (3)	0.028 (2)	0.0250 (19)	-0.007 (2)

C6	0.048 (2)	0.064 (3)	0.080 (3)	0.004 (2)	-0.011 (2)	-0.005 (3)
C3	0.0422 (19)	0.087 (3)	0.060 (3)	0.005 (2)	0.0038 (19)	0.007 (3)
C13	0.0432 (18)	0.055 (3)	0.064 (3)	-0.0049 (16)	-0.0044 (17)	-0.001 (2)

Geometric parameters (\AA , $^\circ$)

Fe1—C1	1.789 (5)	C8—C9	1.373 (4)
Fe1—C2	1.786 (4)	C10—C9	1.368 (5)
Fe1—C3	1.788 (5)	C10—C11	1.378 (5)
Fe1—Fe2	2.471 (2)	C10—H10A	0.9300
Fe1—S1	2.2695 (19)	C11—C12	1.372 (5)
Fe1—S2	2.253 (2)	C11—H11A	0.9300
Fe2—C4	1.789 (5)	C12—H12A	0.9300
Fe2—C5	1.781 (4)	C13—H13A	0.9600
Fe2—C6	1.784 (5)	C13—H13B	0.9600
Fe2—S1	2.2763 (19)	C13—H13C	0.9600
Fe2—S2	2.263 (2)	O3—C3	1.127 (5)
C1—O1	1.131 (4)	O6—C6	1.139 (5)
C2—O2	1.133 (4)	S1—C8	1.787 (3)
C4—O4	1.140 (5)	S2—C9	1.779 (3)
C5—O5	1.135 (5)	S3—C7	1.759 (4)
C7—C12	1.385 (5)	S3—C13	1.790 (4)
C8—C7	1.385 (4)		
C2—Fe1—C3	90.77 (19)	C8—S1—Fe1	101.39 (13)
C2—Fe1—C1	98.59 (17)	C8—S1—Fe2	100.67 (13)
C3—Fe1—C1	99.1 (2)	Fe1—S1—Fe2	65.86 (5)
C2—Fe1—S2	90.09 (15)	C9—C8—C7	120.6 (3)
C3—Fe1—S2	159.76 (15)	C9—C8—S1	115.9 (2)
C1—Fe1—S2	100.74 (14)	C7—C8—S1	123.4 (2)
C2—Fe1—S1	157.30 (13)	C9—C10—C11	117.3 (3)
C3—Fe1—S1	90.84 (14)	C9—C10—H10A	121.3
C1—Fe1—S1	103.50 (13)	C11—C10—H10A	121.3
S2—Fe1—S1	80.80 (5)	O2—C2—Fe1	178.5 (4)
C2—Fe1—Fe2	100.45 (13)	C10—C9—C8	122.1 (3)
C3—Fe1—Fe2	103.00 (16)	C10—C9—S2	122.0 (3)
C1—Fe1—Fe2	150.44 (12)	C8—C9—S2	115.9 (2)
S2—Fe1—Fe2	57.01 (5)	O5—C5—Fe2	177.1 (4)
S1—Fe1—Fe2	57.20 (5)	O1—C1—Fe1	178.4 (4)
C5—Fe2—C6	92.06 (19)	C8—C7—C12	117.4 (3)
C5—Fe2—C4	98.5 (2)	C8—C7—S3	118.3 (2)
C6—Fe2—C4	100.1 (2)	C12—C7—S3	124.3 (2)
C5—Fe2—S2	87.98 (13)	C12—C11—C10	121.5 (3)
C6—Fe2—S2	153.34 (15)	C12—C11—H11A	119.3
C4—Fe2—S2	106.31 (16)	C10—C11—H11A	119.3
C5—Fe2—S1	161.32 (14)	C11—C12—C7	121.0 (3)
C6—Fe2—S1	91.81 (15)	C11—C12—H12A	119.5
C4—Fe2—S1	98.82 (15)	C7—C12—H12A	119.5
S2—Fe2—S1	80.45 (5)	O4—C4—Fe2	177.5 (5)
C5—Fe2—Fe1	104.41 (14)	O6—C6—Fe2	178.4 (4)

C6—Fe2—Fe1	97.78 (16)	O3—C3—Fe1	178.5 (5)
C4—Fe2—Fe1	150.30 (13)	S3—C13—H13A	109.5
S2—Fe2—Fe1	56.64 (3)	S3—C13—H13B	109.5
S1—Fe2—Fe1	56.94 (5)	H13A—C13—H13B	109.5
C7—S3—C13	103.30 (16)	S3—C13—H13C	109.5
C9—S2—Fe1	101.52 (13)	H13A—C13—H13C	109.5
C9—S2—Fe2	101.73 (12)	H13B—C13—H13C	109.5
Fe1—S2—Fe2	66.35 (4)		

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C7—C12 ring.

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C13—H13A—Cg1 ⁱ	0.96	2.69	3.590 (5)	157

Symmetry code: (i) $-x+1, y+1/2, -z+3/2$.